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SOLUBILIZATION AND MICROEMULSIFICATION OF DNAPLS USING EDIBLE SURFACTANTS PREPRINT (Code 20)

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Solubilization and Microemusification of DNAPLs Using Edible Surfactants

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ABSTRACT

This research demonstrated that solubilization (micellar partitioning) and formation of a middle phase microemulsion with chlorinated organics (PCE, TCE, and trans 1,2-DCE) were feasible using edible surfactants (those with FDA direct food additive status). Micellar partitioning coefficients with edible surfactants were observed to be comparable to values previously reported for other surfactants. Obtaining a middle phase microemulsion was observed to be a function of the surfactant structure and was achieved by varying the cosurfactant concentration. Solubility enhancement in the middle phase systems (microemulsification) was observed to be at least one order of magnitude more efficient than solubilization in micelles for the same surfactant concentration, but was observed to be much more sensitive to the surfactant system, the specific contaminant, and aquifer conditions. Preliminary results are shown to indicate the impact of temperature and hardness (multivalent ion concentrations) on middle phase systems and to indicate the need to consider these and additional factors for successful design and implementation of surfactant enhanced subsurface remediation.

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INTRODUCTION

Chlorinated hydrocarbons are ubiquitous groundwater contaminants due to their widespread use as organic solvents and cleaners/degreasers. The immiscibility of chlorinated organics with groundwater results in their occurrence in the subsurface as residual (trapped) phases (thus the term dense nonaqueous phase liquids--DNAPLs). Water solubilities of these chlorinated organics can be several orders of magnitude above their drinking water standards. Remediation of residual saturation of DNAPL can require hundreds to thousands of pore volumes using conventional pump and treat methods. This is also true for strongly hydrophobic compounds that will exhibit high levels of sorption with the subsurface medium.

The inefficiency of conventional pump and treat methods for remediation of residual saturation or highly hydrophobic organics has been addressed by several recent reviews. Keeley (1989) provides an excellent discussion of factors impacting pump and treat remediation efforts. In discussing limitations of pump and treat remedial efforts, the desorption of contaminants from media surfaces and liquid partitioning of immiscible contaminants are enumerated as limiting factors. Haley, et al. (1991) evaluated 19 ongoing and completed groundwater remediation systems for effectiveness in subsurface remediation. The analysis of these sites suggested that containment of groundwater contaminants was usually achieved; however, the removal of contaminants from the subsurface was usually slower than anticipated. Factors limiting remediation included high sorption of organics and the presence of residual saturation. The authors recommended that methods be evaluated to further enhance the effectiveness and efficiency of extracting these contaminants from the subsurface.

Palmer and Fish (1992) discuss chemical enhancements to pump and treat remediation, including: complexing agents, cosolvents, surfactant enhanced solubilization and mobilization, oxidation/ reduction agents, precipitation/dissolution reagents, and ionization reagents. An EPA-

sponsored workshop which enumerated a variety of technologies for remediation of subsurface DNAPL contamination (including the benefits and limitations of each) included surfactant enhanced subsurface remediation as a process meriting further study (USEPA, 1992). From the above references it is apparent that surfactants are excellent candidates for expediting the dissolution/desorption of subsurface contamination by organic compounds.

An obvious obstacle to widespread implementation of surfactant enhanced subsurface remediation will be gaining regulatory approval for the injection of surfactants into the subsurface. This obstacle is of course common to all chemical amendments being considered for subsurface remediation. In an effort to increase the likelihood of gaining regulatory approval, this research will focus on the use of surfactants with U.S. Food and Drug Administration direct food additive status. Surfactants with this status are common in food products and other consumer goods.

LITERATURE REVIEW

Much research has been conducted on the migration of DNAPLs released to the subsurface. Several recent publications include: Wilson, et al. (1989), Kueper, et al. (1989), Feenstra (1990), Cherry et al. (1990), Mercer and Cohen (1990), and Huling and Weaver (1991). Fundamentals of DNAPL migration in the subsurface are summarized below.

Depending on the volume and nature of the DNAPL release, the contaminant(s) may be trapped (occur as residual saturation) in the unsaturated zone and the saturated zone. In the presence of residual saturation, groundwater remediation without amendments may require extraction of hundreds to thousands of pore volumes or more, depending on the contaminant. Surfactants can significantly increase the "aqueous" solubility of the contaminants and thus equally decrease the pore volumes necessary for remediation by a similar factor. Surfactant

enhanced remediation is typically discussed in terms of two discrete mechanisms: solubilization (partitioning of the contaminant into the oil-like interior of surfactant micelles) and mobilization (microemulsification -formation of middle phase microemulsions with a concomitant achieving of a minimum in DNAPL/groundwater interfacial tension which results in release of trapped DNAPL from media pores).

Figure 1 shows a phase diagram as a function of changing HLB for the surfactant system (Shinoda and Friberg, 1986). The bottom portion of the diagram (high HLB number) corresponds to a system with an excess oil phase, surfactants in the water phase, and oil solubilized into the core of the micelles in the water phase. The top portion of this diagram (low HLB number) demonstrates an excess water phase with reverse micelles in the oil phase; in this case we have water solubilized into the polar core of the reverse micelle. What is observed in the transition between these two extremes is normal micelles followed by swollen micelles followed by the appearance of a third phase (a middle phase denoted as D), and finally reverse swollen micelles, then reverse micelles. Obtaining a middle phase microemulsion thus requires a proper balance of the surfactant system as well as preventing the formation of any structured mesophases (e.g., liquid crystal or gel).

Bourrell and Chambu (1983) discuss factors affecting the realization of middle phase systems. Figure 2 (adapted from Bourrell and Chambu, 1983) illustrates the interactions of surfactant membrane (C) with oil (O) and water molecules (W). As shown in Figure 2, the molecular interactions promoting miscibility between C and O are A_{CO} and A_{CW}, respectively. The A_{CO} and A_{CW} terms can be split into the lipophilic (L) and hydrophilic (H) type interactions: $A_{CO} = A_{LCO} + A_{HCO}$ and $A_{CW} = A_{LCW} + A_{HCW}$. The interactions promoting segregation of the components as separate phase are A_{OO} and A_{WW}. The R-ratio (or F-ratio) modified from Winsor (1948; 1954) is defined as the tendency for the surfactant to disperse into oil ($= A_{CO} - 1/2A_{OO} -$

$1/2A_{LL}$), divided by its tendency to dissolve in water (= A_{CW} - $1/2A_{WW}$ - $1/2A_{HH}$). Factors which alter these interactions will alter the distribution of the surfactant between the phases (the R-ratio value) and will affect the location of the system on the phase diagram. Balancing these interactions prompts accumulation of surfactant at the oil/water interface and middle phase formation (R = 1 is optimum).

Various means exist for adjusting the balance of the surfactant system. For nonionic surfactants, adjustment of the temperature will alter the surfactant/solvent interactions and can be used to cause phase inversion (converting from a normal micelle to a balanced system to a reverse micelle system by increasing temperature). For ionic surfactants, adjustment of the salinity (NaCl) or hardness ($CaCl_2$) of the aqueous phase can alter the interactions and cause phase inversion. Figure 3 (adapted from Bourrell and Chambu, 1983) is an example of transitioning from a normal micelle to a swollen micelle (Winsor Type I microemulsion) to a middle phase microemulsion (Winsor Type III system) to a reverse swollen micelle system (Winsor Type II system). In this case, sodium dodecyl sulfate (SDS) and pentanol are used as surfactant and cosurfactant, respectively. For a given weight percent of surfactant and cosurfactant (ordinate) and scanning across sodium chloride concentrations (abscissa), one transitions from a Type I through a Type III to a Type II system. As shown in Figure 3, the type of system (I, III, or II) is determined by the value of the R-ratio. For $R << 1$, the characteristic system is Type I, and the corresponding system is Type II for $R >> 1$. Moreover, it is observed that Type III behavior is realized for R values in the vicinity of one. The R-ratio is unity when the middle phase contains equal volumes of water and oil. Thus, Figure 3 is often referred to as a salinity scan. Balancing the surfactant using salinity is the common approach utilized in surfactant enhanced oil recovery. However, such an approach is not as amenable to subsurface remediation methods due to the high dosage of NaCl. In addition,

the traditional cosurfactants (medium chain length alcohol, C_4 or above) for destabilizating the liquid crystalline phase may not be useful due to their toxicity (see Friberg and Kayali, 1991); these authors suggested the destabilization could be obtained by the use of hydrotropes. A large number of hydrotropes are allowed in food products. Alteration of the balance of the system in the research presented here will utilize mixed surfactant systems and/or a cosurfactant (hydrotrope) systems. For additional discussion of surfactant enhanced oil recovery research, the reader is referred to Shah (1981), Bourrel and Schechter (1988), and Schramm (1992), to name but a few of the excellent discussions on this subject.

Surfactant enhanced environmental remediation research to date has tended to emphasize the solubilization mechanism using surfactants irrespective of FDA food additive status. A brief review of some of this research is presented below. Vignon and Rubin (1989) discussed optimization of the surfactant systems for enhanced solubilization of sorbed anthracene and biphenyl using alkyl and alkylphenyl ethoxylated surfactants. Abdul et al. (1990) evaluated four groups of surfactants for the solubilization of automatic transmission fluid from shallow sandy aquifer material. The percent recovery increased from 23% by washing with sand with water alone, to 80% by washing with ethoxylated alcohol surfactants.

Valsaraj and Thibodeaux (1989) evaluated the micellar partitioning coefficients for sodium dodecyl sulfate (ionic surfactant) and eleven hydrophobic nonpolar organics. They observed a correlation between the hydrophobicity of the contaminant (K_{ow}) and the micellar partitioning coefficient. Edwards et al. (1991, 1992) discussed the use of alkyl and alkylphenyl ethoxylated surfactants (nonionic surfactants) to enhance the solubilization of PAHs. They also observed a correlation between the partitioning coefficient and the contaminant hydrophobicity, with the nonionic surfactants evidencing higher partitioning coefficients (as commonly observed in the solubilization literature). West (1992) utilized the same surfactants as Edwards et al.

(1991) for solubilization of chlorinated organics (PCE, TCE, and 1,2-DCE) and found a similar relationship between the micellar partitioning coefficient and the K_{ow} of the compounds.

Fountain (1992) evaluated surfactant-enhanced remediation of chlorinated organics at two field sites: Borden, Ontario and Corpus Christi, Texas. The target compound at the Borden, Ontario research site was PCE and at the Corpus Christi, Texas site was carbon tetrachloride from a fluorocarbon manufacturing facility. Good solubilization was realized at both sites without evidence of significant vertical migration of the DNAPL. The author utilized an edible surfactant (ethoxylated sorbitan ester) at the Corpus Christi site. Abdul et al. (1992) conducted a field scale study to evaluate surfactant enhanced remediation of PCB contamination in the unsaturated zone. A ten-foot diameter by five-foot deep test plot was evaluated within the contamination zone. About 10% of the contaminant mass was solubilized in approximately 6 pore volumes. The above references indicate the need for research focusing on the use of edible surfactants for surfactant enhanced solubilization and microemulsification. The hypotheses of this research are that edible surfactants can effectively solubilize chlorinated organic compounds and that mixtures of edible surfactants can produce middle phase microemulsion systems with chlorinated organics (DNAPLs). The objectives of this research are to establish that it is feasible to use edible surfactants for enhanced remediation, to provide a preliminary comparison of the efficiency of these edible surfactants with surfactants previously investigated, and to enumerate additional issues that need to be evaluated prior to full scale implementation of this technology.

MATERIALS AND METHODS

The chlorinated organics evaluated in this research were tetrachloroethylene (PCE), trichloroethylene (TCE), and trans-1,2-dichloroethylene (1,2 DCE). Table 1 lists some common

parameters for these chlorinated organic compounds. These compounds were selected based on their ubiquitous occurrence as subsurface contaminants in the form of residual saturation, their range in hydrophobicity, etc. PCE and TCE were purchased from Fisher Scientific, and 1,2 DCE was obtained from Eastman Kodak Company.

The surfactants evaluated in this research were selected based on their status as FDA direct food additives and the HLB of the surfactants (see Table 2). Note that the surfactants are combinations of fatty acids and sugars. The S-MAZ surfactants and T-MAZ surfactants are sorbitan esters and polyethyloxylated sorbitan esters, respectively (with ethylene oxide groups ranging from 20 to 80 as noted in Table 2). The HLB values were not found for several surfactants; they are included in the table based on their relative water/oil solubility compared to the other surfactants utilized. The source of the surfactants are also included in Table 2 and all surfactants were utilized as received. Synthetic groundwater was used for preparing all aqueous phase solutions; their compositions include calcium 16, sodium 4.6, potassium 23.5, bicarbonate 48.8, chloride 21.3, and sulfate 9.6 (all on a mg/L basis). Polarizing filters (Hoya 55 mm PL-Circular No. 3639, Japan) were used for checking the birefringence phenomenon indicative of the presence of liquid crystals.

Solubilization studies were conducted in batch systems (40 ml EPA vials obtained from Fisher) by the excess additive method (Dunn et al., 1985; Kandori and Schechter, 1990). A surfactant solution of 40 ml was used to minimize the head space losses. Different amounts of chlorinated organics were added by microliter syringe into reactors with constant surfactant concentration. Samples were shaken using autoshaker for 24 hrs and were equilibrated at 15 $\pm$ 0.1 °C for one week before checking results. Solubilization limits were determined by visual inspection to see if any excess phase existed (Dunn et al., 1985; Kandori and Schechter, 1990). Middle phase microemulsion studies were conducted in 10 ml pipette systems sealed to prevent

volatilization losses (Saito and Shinoda, 1970; Reed and Healy, 1977). Five mls of chlorinated hydrocarbon and 5 mls of aqueous solution with predetermined amounts of surfactant/cosurfactant dissolved were added and sealed. Samples were vigorously shaken several times by hand, and were equilibrated at 15 °C. The phase volumes were monitored by visual inspection as a function of time. In general, middle phase microemulsions showed separation of excess phase relatively rapidly (minutes to hours).

RESULTS

Solubilization by single surfactant systems were conducted for SDS and three of the T-MAZ surfactants. Figure 4 summarizes the solubilization of the three chlorinated organics with T-MAZ 60 at 15 °C. It is observed that at concentrations above the critical micelle concentration, CMC (ca. 0.0213 mM), the aqueous phase concentration of the chlorinated organics increases linearly. This is in keeping with classical solubilization (partitioning) theory. The slope of this line is the molar solubilization ratio (MSR) which indicates the moles of DNAPL per mole of surfactant in micelles. The MSR can be utilized to determine the micellar/aqueous phase partitioning coefficient (K_m) (Edwards et al., 1991; West, 1992); values of K_m are summarized in Table 3. Table 3 also includes the solubilization parameters for T-MAZ 20, T-MAZ 28, and SDS. It is observed from Table 3 that the more hydrophobic contaminant (PCE) evidences the higher partitioning coefficient between the micelles and the aqueous phase. The partitioning coefficient decreases as the hydrophobicity of the organic compound decreases (from PCE to TCE to 1,2-DCE). It is also observed that for a given organic compound, the partitioning coefficient is higher for the nonionic surfactants than for the ionic surfactant (the T-MAZ surfactants and SDS, respectively). The partitioning coefficients are similar for T-MAZ 20 and T-MAZ 60, both having 20 ethylene oxide groups. T-MAZ 28

is observed to have partitioning coefficients between the other T-MAZ surfactants and SDS. It is hypothesized that the added polarity of the T-MAZ 28 surfactant (with 80 ethylene oxide groups) is responsible for this behavior.

It is noted from Figure 4 that at surfactant concentrations of 50 millimolar the plot exhibits nonlinearity. The plots are linear up to ca. 15 mM. Visual observations of cloudiness at the higher surfactant concentrations suggests that the surfactant has exceeded the cloud point. This illustrates the trade off between ionic and nonionic surfactants. While nonionic surfactants have lower CMCs, (more of the surfactants are in micelles at a given concentration), nonionic surfactants can not achieve the high water solubilities of ionic surfactants.

Partitioning coefficients using these edible surfactants are also compared in Table 3 to results of West (1992) who utilized alkylphenyl ethoxylated surfactants (with eight to twelve alkyl groups and four to twelve ethoxy groups). The C_{18} (T-MAZ 60) nonionic surfactants utilized in our research would be expected to have slightly higher K_m values than the C_8 to C_{12} surfactants evaluated by West (1992). This demonstrates that solubilization with edible surfactants is as effective as that obtained using surfactants without direct food additive status (as anticipated from the fundamentals of solubilization).

Initial studies attempting to achieve middle phase microemulsions with combinations of food additive surfactants only were unsuccessful. In these initial studies, the HLB of the surfactant mixture was varied from 2.1 to 40. Phase inversion was observed in this HLB range (transition from Type I to Type II system); however, rather than a clear middle phase, a milky phase (not a liquid crystal phase) was observed in the transition region. It was at this time that use of a branch tailed surfactant and a cosurfactant (hydrotrope) was decided upon. Aerosol OT (AOT) (see Table 2) and sodium mono- and di-methyl naphthalene sulfonate (SMDNS) were selected as branched surfactant and cosurfactant, respectively. Using these surfactants, a middle

phase microemulsion (a separate translucent liquid phase between the water phase and the DNAPL phase) was observed in the transition region. The resulting middle phase was not a liquid crystal phase as no birefrigence phenomenon was observed for the middle phase using polarizing filters. The transition was achieved by maintaining a constant AOT concentration and varying the SMDNS concentration. These results confirm that obtaining a middle phase system is a function of surfactant structure, etc. (Bourrel and Schechter, 1988).

Figure 5 shows a phase diagram for 1,2-DCE using AOT and SMDNS as the surfactant system. It is observed that at low SMDNS concentration the surfactant system is not balanced and the AOT has partitioned into the oil phase, creating a Type II system. Increasing the SMDNS concentration enhances the surfactant balance (increases the affinity of the AOT for the interface), and results in a middle phase system. At yet higher SMDNS concentrations, the system is over optimized and the surfactants reside in the water phase (Type I system). Thus we observe that at the intermediate SMDNS concentration, the surfactant balance is achieved and a Winsor Type III system is realized. It is observed that in this system, the range over which a middle phase is observed is approximately 0.14 wt % of SMDNS. Table 4 summarizes the centroid concentration and range of concentrations of SMDNS in which middle phase systems were achieved for the three chlorinated organics.

In comparing the DNAPL uptake efficiency of the solubilization and the microemulsification mechanisms, Table 5 documents the enhancements by these two mechanisms for a common weight percent of surfactant for solubilization with T-MAZ 60 and for microemulsion formation using AOT and SMDNS. As observed from Table 5, the enhancement is two orders of magnitude for PCE via the solubilization and three and one-half orders of magnitude via the microemulsification mechanism (based upon solubilization in the middle phase microemulsion). It is observed that for 1,2-DCE the enhancement by solubilization is

approximately one order of magnitude and it is two orders of magnitude for the microemulsification. The dramatic increase in efficiency of microemulsification versus solubilization is thus obvious. However, the microemulsification system is much more sensitive to changes in surfactant concentrations, hydrotrope concentration, hardness, etc. Also, at the low DNAPL/groundwater interfacial tensions which occur in the presence of middle phase microemulsions, vertical migration of mobilized DNAPLs may render this approach undesirable (Fountain, 1992). On the other hand, horizontal migration of mobilized DNAPL is also feasible and could dramatically accelerate a remediation project. Our contention, therefore, is that both mechanisms should continue to be evaluated in light of the potential advantages and disadvantages of each. Table 5 also demonstrates that surfactant enhanced subsurface remediation (via both solubilization and microemulsification) will be most advantageous for the more hydrophobic compounds.

The data presented above demonstrates that surfactant enhanced solubilization and microemulsification are feasible using edible surfactants (those with FDA direct food additive status). Thus the hypotheses of this research have been verified. Additional issues, however, must be addressed prior to successful and economical implementation of surfactant enhanced subsurface remediation using edible surfactants in full scale systems. Factors that must be considered include the impact of temperature and salinity upon the middle phase systems, and the impact of surfactant sorption and precipitation on the economics of both systems (Rouse et al., 1993). Finally, since surfactant recovery and reuse is critical to the economics of remediation using solubilization, effluent processing must also be considered.

As an indication of the impact of temperature and hardness on middle phase systems, Figures 6 and 7 indicate the impact of temperature upon the middle phase systems for PCE and the impact of hardness upon the middle phase systems for TCE, respectively. It is observed

from Figure 6 that at higher temperature, less SMDNS is required to achieve the middle phase system. This is consistent with the surfactant balance described earlier; at higher temperature the ionic surfactant will be more water soluble, and thus less SMDNS is necessary to achieve the desired HLB balance. In Figure 7 it is observed that at higher values of hardness, more SMDNS is required to maintain the surfactant balance. This is as anticipated because the increased calcium concentration will tend to drive the ionic AOT into the oil phase, and thus additional SMDNS is required to maintain the surfactant balance and retain the middle phase microemulsion. Figures 6 and 7 are presented here to reinforce the point of the sensitivity of these systems to aquifer conditions, to amplify the need for additional research, and to alert potential users of this technology to dangers associated with attempting to apply this technology without proper site specific research and design efforts. Future publications will further expand upon these and other issues important to the technical and economical feasibility of full scale implementation of surfactant enhanced subsurface remediation.

CONCLUSIONS

Surfactants are being evaluated as chemical amendments for enhancing subsurface remediation. A likely obstacle to implementation of this technology is obtaining regulatory approval for introduction of chemical amendments. Thus, this research has focused on the use of edible surfactants (those with FDA direct food additive status). This research demonstrated that solubilization in micelles and formation of a middle phase microemulsion were feasible using edible surfactants (those with FDA direct food additive status) and DNAPL (PCE, TCE, and trans 1,2-DCE). Micellar partitioning coefficients with edible surfactants were observed to be a function of contaminant hydrophobicity and to be comparable to values previously reported for other surfactants. Highly ethoxylated nonionic surfactants were observed to have partitioning

coefficients between those of ionic surfactants and less ethoxylated nonionics.

Middle phase microemulsions were successfully achieved by varying the concentration of a cosurfactant. Obtaining a middle phase microemulsion was observed to be a function of the surfactant structure (branch tailed surfactants were utilized in this research) and cosurfactant (hydrotrope). The microemulsification was observed to be one order of magnitude more efficient than solubilization in term of uptake of DNAPL for the same surfactant concentration. Achieving a middle phase microemulsion, however, was observed to be much more specific to the contaminant type and sensitive to variations in system parameters.

Preliminary results indicate the impact of temperature and salinity on middle phase systems. Decreasing temperature and increasing hardness required additional cosurfactant to maintain a balanced system (retain the middle phase system). These results illustrate the need to consider these and additional factors for successful design and implementation of surfactant enhanced subsurface remediation.

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Table 1: Chlorinated organics properties used in this study

Name	Density (g/cm^3)	Absolute Viscosity (cp)	Vapor Pressure (mm Hg)	Vapor Density Relative to Dry Air	Solubility (mg/L)	NYSDEC Drinking Water/GW Standard (mg/L)	K_{ow}	Interfacial Tension (dyne/cm)
Tetrachloroethylene (PCE)*	1.62[a]	0.90	14	1.09	200	0.002	3.98×10^2	44.4[b]
Trichloroethylene (TCE)*	1.46	0.57	58	1.27	1100	0.005	2.40×10^2	34.5
trans-1,2-Dichloroethylene (1,2 DCE)′	1.26	0.40	326	2.01	6300	0.05	3.02	30

Notes: properties at 20 °C unless specified
[a] from Weast, 1986.
[b] properties at 25 °C
* from Fisher Scientific
′ from Eastman Kodak
NYSDEC- New York State Department of Environmental Conservation
Data adapted from Schwille, 1988; Feenstra and Cherry, 1988; Mercer and Cohen, 1990

Table 2: Surfactant properties used in this study

Name	HLB	MW	Type
Sodium mono and dimethyl naphthalene sulfonate (SMDNS)[a]	NA	260	A
Sodium dodecyl sulfate (SDS)[b]	40	288	A
POE(80) sorbitan monolaurate (T-MAZ-28)[c]	19.2	3866	N
POE(20) sorbitan monolaurate (T-MAZ-20)[c]	16.7	1226	N
POE(20) sorbitan monostearate (T-MAZ-60)[c]	14.9	1310	N
Bis-2-ethylhexyl sodium sulfosuccinates (Aerosol OT)[d]	NA	445	A
POE(20) sorbitan tristearate (T-MAZ-65)[c]	10.5	1842	N
Sodium stearoyl-2-lactylate[e]	10	450	A
Calcium stearoyl-2-lactylate[e]	NA	894	A
Triglycerol monooleate (MAZOL-PGO-31K)[c]	6.2	536	N
Sorbitan monooleate (S-MAZ-80K)[c]	4.6	428	N
Glycerol monooleate (MAZOL-300K)[c]	3.8	356	N
Sorbitan trioleate (S-MAZ-85K)[c]	2.1	956	N

[a]from Witco
[b]from Fisher Scientific
[c]from PPG/Mazer Chemicals
[d]from American Cyanamid
[e]from American Ingredients

Table 3: Molar Solubilization Ratios (MSR) and Partitioning Coefficients (K_m)

Organic	Surfactant	MSR	log K_m*
PCE	SDS	0.39	4.50
	T-MAZ 28	0.45	4.55
	T-MAZ 20	2.27	4.90
	T-MAZ 60	3.15	4.94
TCE	SDS	0.34	3.27
	T-MAZ 28	1.68	3.66
	T-MAZ 20	3.29	3.75
	T-MAZ 60	3.95	3.77
1,2-DCE	SDS	1.37	2.76
	T-MAZ 28	2.46	2.85
	T-MAZ 20	7.49	2.95
	T-MAZ 60	6.91	2.94

* $K_m = [55.4/S_{DNAPL,CMC}]x[MSR/(1+MSR)]$

** $S_{DNAPL,CMC}$ (= the solubilities of the DNAPLs at CMC) are $4.86x10^{-4}$, $7.54x10^{-3}$, $5.51x10^{-2}$ mole/L for PCE, TCE, and 1,2 DCE respectively, as determined in this study.

*** From West (1992) range of Km values for PCE, 4.14 to 4.47; TCE, 3.49 to 3.72; and 1,2 DCE, 2.97 to 3.01.

Table 4: Summary for the middle phase microemulsion for three chlorinated organics

Name	Centroid Concentration of SMDNS for Middle Phase (wt %)	Range of SMDNS Concentration for Middle Phase Δ [SMDNS] (wt %)	Volume of Middle Phase at Centroid Concentration of SMDNS (ml)
PCE	1.40	0.30	2.3
TCE	2.43	0.15	1.2
1,2 DCE	2.19	0.14	2.0

Table 5: Comparison of Surfactant Enhanced DNAPL Remediation via Solubilization and Microemulsification Mechanisms

DNAPL	GW Solubility (mM)	Solubilization (T-MAZ 60*) (mM)	Microemulsification (AOT & SMDNS**) (mM)***
PCE	0.486	102	3730
TCE	7.54	112	4520
1,2-DCE	55.1	390	5750

* ca. 6.5 wt % surfactant

** ca. 5.0 wt % surfactant (AOT and SMDNS)

*** ca. based on the volume changes of water and DNAPL phases

Figure 1: Phase Diagram for Oil/Water/Surfactant System as a Function of HLB System. (Adapted from Shinoda and Friberg, 1986).

Figure 2: Surfactant Interactions in Oil/Water/Surfactant System. (Adapted from Bourrel and Chambu, 1983).

Figure 3: Optimization Diagram for Achieving Winsor Type I - IV Systems as a Function of Changing Salinity and Surfactant Concentrations. (Adapted from Bourrel and Chambu, 1983).

Figure 4: Solubilization of DNAPLs (PCE, TCE, and 1,2 DCE) in T-MAZ 60 @ 15 °C.

Figure 5: Phase Diagram for 1,2 DCE as a Function of SMDNS Concentration @ 15 °C and for 0.5 wt% AOT.

Figure 6: Phase Diagram for PCE for AOT and SMDNS at Two Temperatures.

Figure 7: Phase Diagram for TCE at 15 °C for AOT and SMDNS for Two Calcium Values.

FIG1 SHIAU

TOP

FIG 2 SHIAU

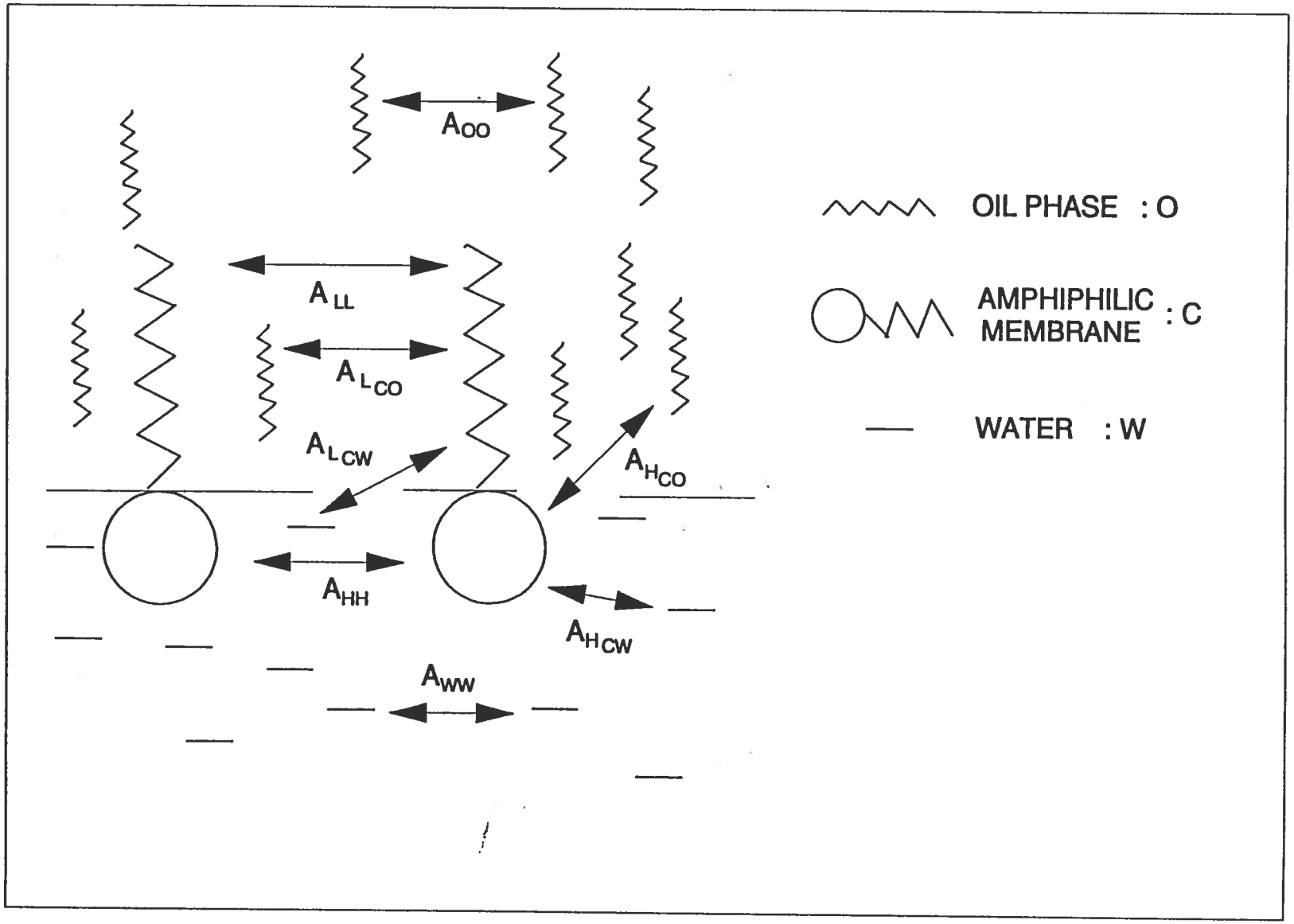

A_{OO}
A_{LL}
A_{LCO}
A_{LCW}
A_{HCO}
A_{HH}
A_{HCW}
A_{WW}
OIL PHASE : O
AMPHIPHILIC MEMBRANE : C
WATER : W

FIG 3 SHIAU TOP

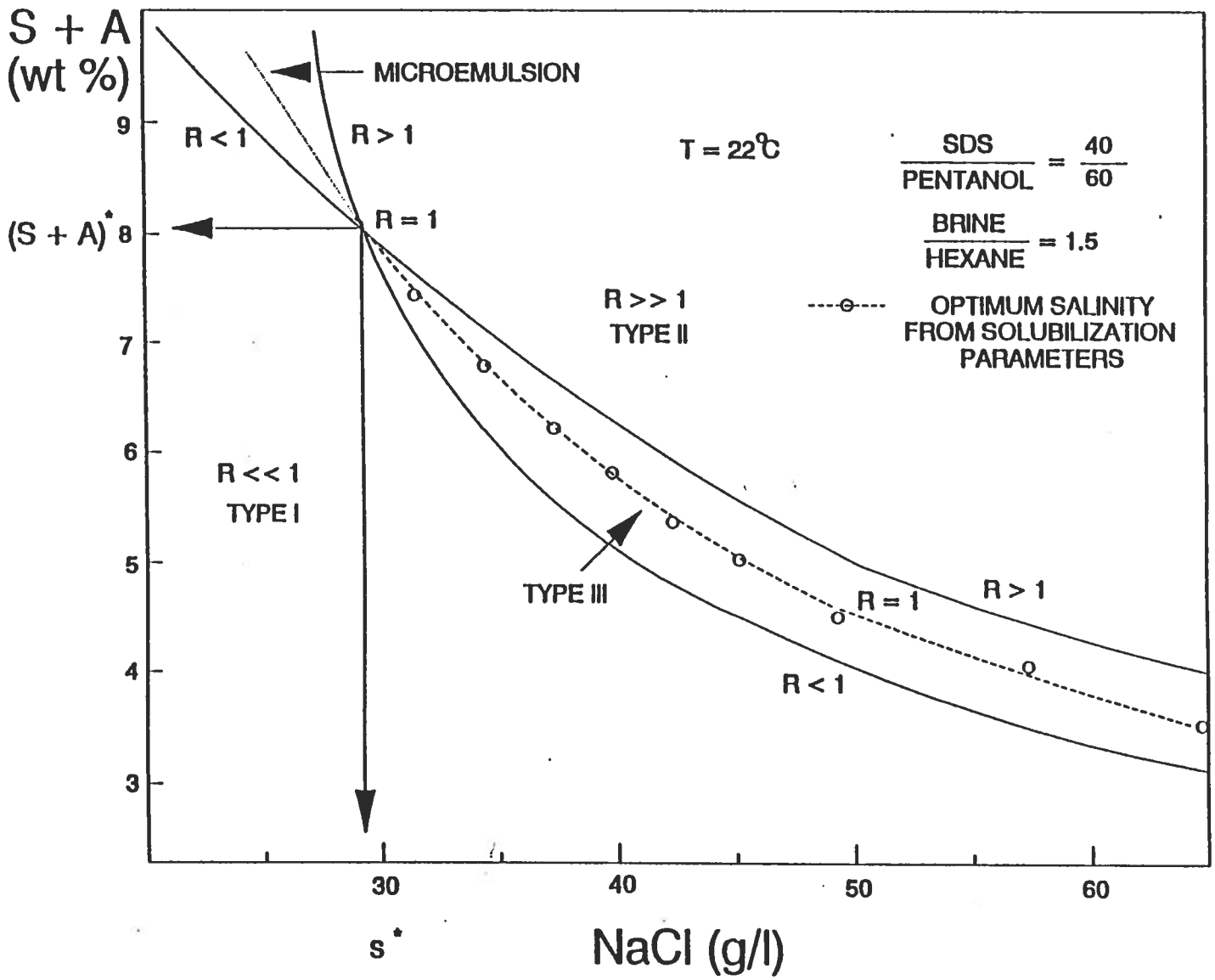


FIG 4 SHIAU TOP

SOLUBILITY OF THE DNAPLS

T-MAZ 60 @15 C

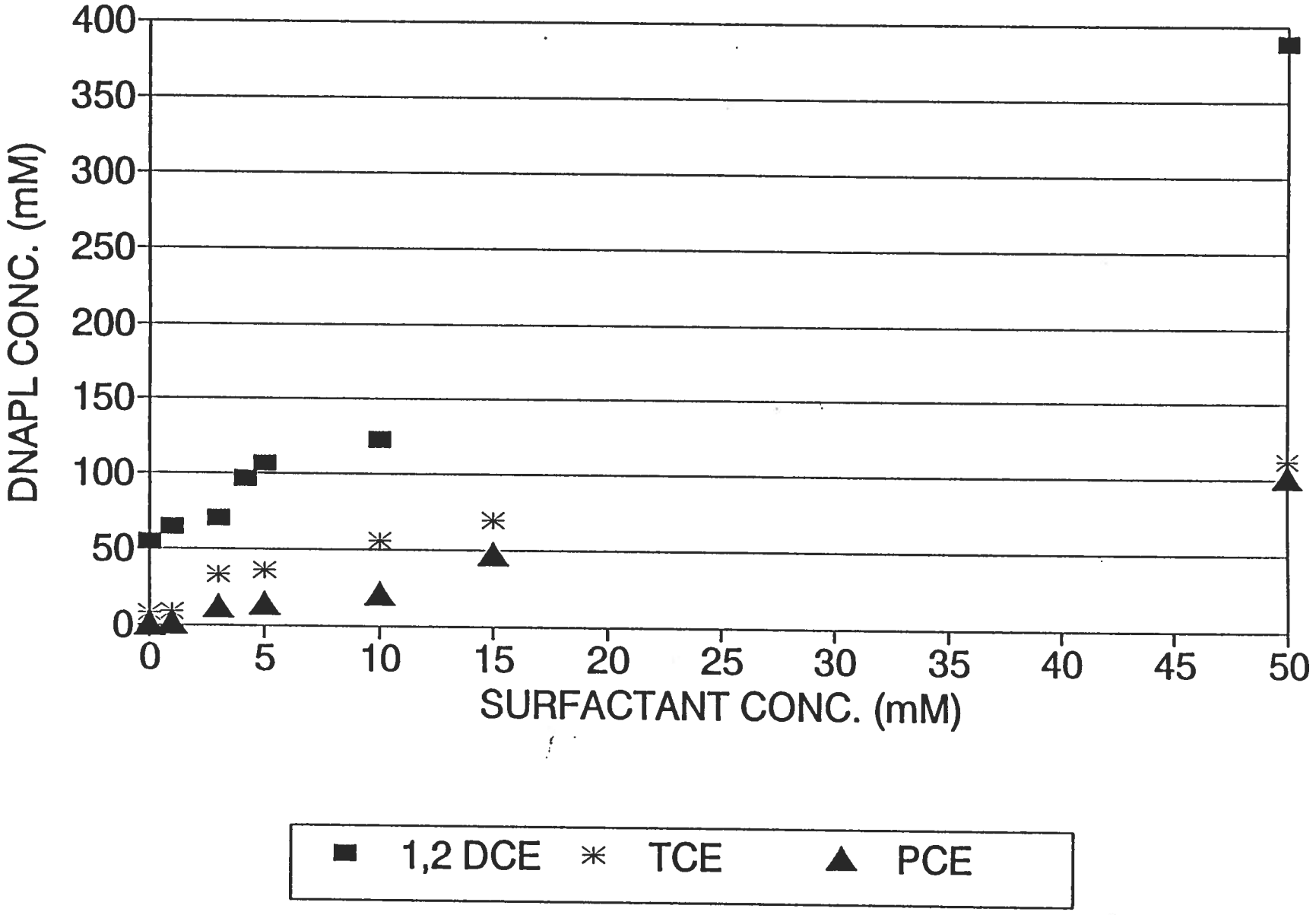


FIG 5 SHIAU TOP

PHASE-VOLUME DIAGRAM FOR 1,2DCE @15 C.

AOT= 0.5 wt%, W/O= 1

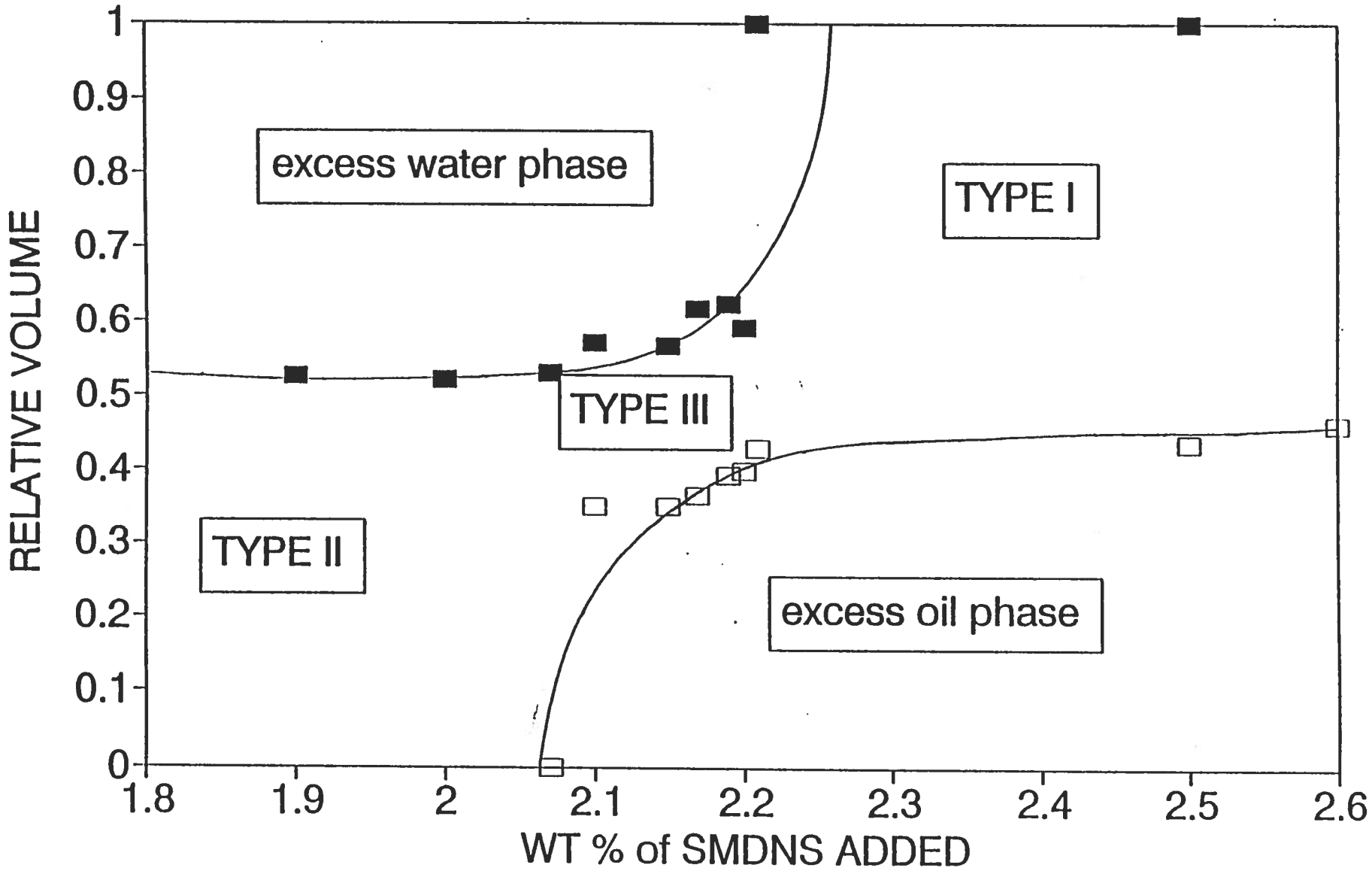
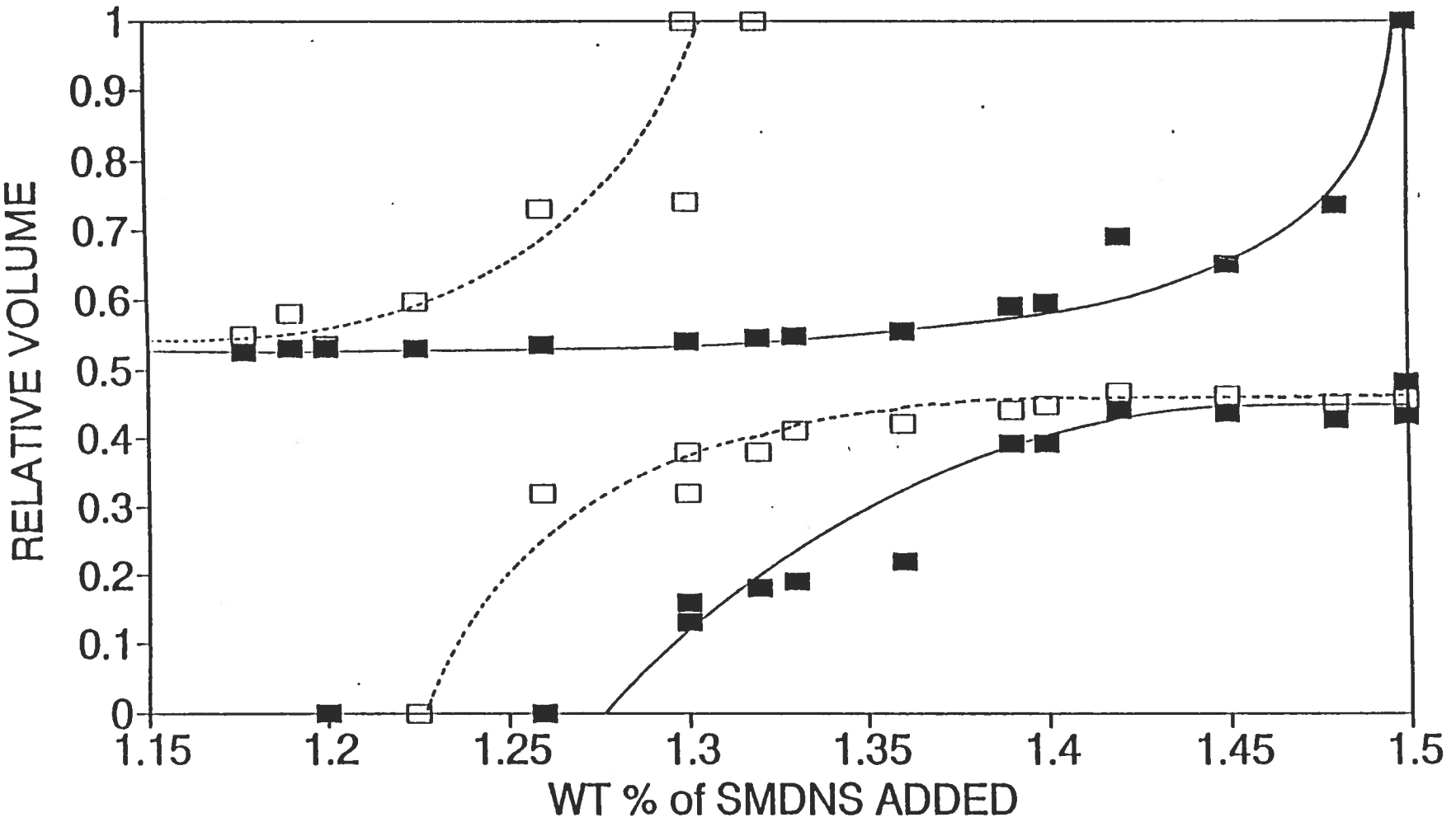


FIG 6 SHIAU TOP

PHASE-VOLUME DIAGRAM FOR PCE

AOT= 0.5 wt%, W/O= 1

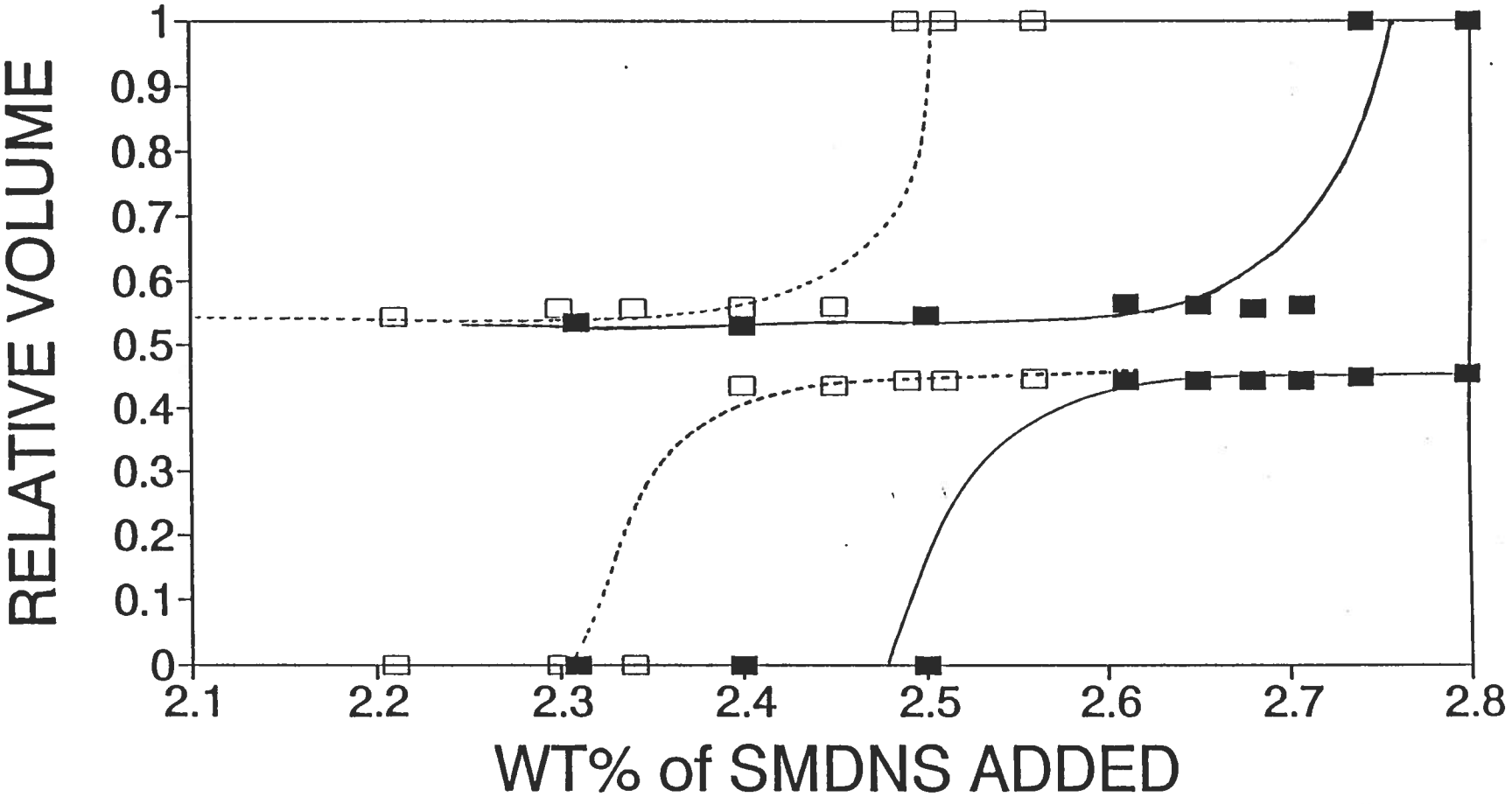


□ TEMP= 25 C ■ TEMP= 15 C

FIG 7 SHEET Top

PHASE-VOLUME DIAGRAM FOR TCE

AOT= 0.5 wt%, W/O= 1



□ [Ca]= 16 mg/l (GW) ■ [Ca]= 478 mg/l